CHARACTERIZATION OF HYBRID FRP COMPOSITE WITH HYDROTHERMAL EXPOSURE UNDER VARIED AMBIENT CONDITIONS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology

in

Metallurgical and Materials Engineering

By

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Department of Metallurgical and Materials Engineering

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UNDER GUIDANCE OF

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CERTIFICATE

This is to certify that the thesis entitled, "CHARACTERIZATION OF HYBRID FRP COMPOSITE WITH HYDROTHERMAL EXPOSURE UNDER VARIED AMBIENT CONDITIONS" submitted by AJIT PANIGRAHI in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date:

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Metallurgical and Materials Engineering

ABSTRACT

The present experimental study aims at assessing the effect of moisture and temperature on the mechanical properties of hybrid FRP composites. Samples of several Carbon-Glass-Epoxy hybrids were manufactured using hand layup method where the stacking of plies was alternate and the weight fraction of fibre and matrix was kept at 50%-50%. Specimens were cut from the fabricated laminate according to the ASTM D 2344-84(1989) standards. Some of these specimens were kept in the As-Cured condition so as to obtain the base properties. Rest specimens were then subjected to hydrothermal environment at temperature of 60^0C for 24,48,72,96,120 hours. These specimens were divided into groups of five. One group was subjected to cryogenic conditions at -40^0C for 2 hours and the other group was subjected to elevated temperature at 50^0C for 2 hours. These treated samples were then subjected to short beam shear test or 3 point bend test. The ILSS (shear strength) values were then compared with the base values of as cured specimen. Differential scanning calorimetry was done to find the Tg variation. SEM analysis was done to ascertain the mode of failure.

CONTENTS

1. INTRODUCTION

A COMPOSITE MATERIAL is a macroscopic combination of two or more distinct materials, having a recognizable interface between them [1]. Composites are used not only for their structural properties, but also for electrical, thermal, tribological, and environmental applications. It consists of reinforcing stiffer phase and the matrix phase. The resulting composite material has a balance of structural properties that is superior to either constituent material alone. Composites typically have a fiber or particle phase that is stiffer and stronger than the continuous matrix phase and serve as the principal load carrying members. The matrix acts as a load transfer medium between fibers, and in less ideal cases where the loads are complex, the matrix may even have to bear loads transverse to the fiber axis. The matrix is more ductile than the fibers and thus acts as a source of composite toughness. The matrix also serves to protect the fibers from environmental damage before, during and after composite processing [2]. A hybrid composite is a FRP composite which has more than one fiber as a reinforcement phase embedded into a single matrix phase. Hybridization provides the designers with an added degree of freedom in manufacturing composites to achieve high specific stiffness, high specific strength, enhanced dimensional stability, energy absorption, increased failure strain, corrosive resistance as well as reduced cost during fabrication [3]. Composites made of a single reinforcing material system may not be suitable if it undergoes different loading conditions during the service life. Hybrid composites may be the best solution for such applications [4]. Normally, one of the fibers in a hybrid composite is a high-modulus and high-cost fiber such as carbon, boron and the other is usually a low-modulus fiber such as E-glass, Kevlar. The high-modulus fiber provides the stiffness and load bearing qualities, whereas the low-modulus fiber makes the composite more damage tolerant and keeps the material cost low. The mechanical properties of a hybrid composite can be varied by changing volume ratio and stacking sequence of different plies. High-modulus fibers such as carbon, boron are widely used in many aerospace applications because of their high specific modulus. However, the impact strength of composites made of such high-modulus fibers is generally lower than conventional steel alloys or glass reinforced composites. An effective method of improving the impact properties of high-modulus fiber composites is to add some percentage of low-modulus fibers like E-glass. Most composite materials

experience time varying internal disturbance of moisture and temperature during their service life time which can cause swelling and plasticization of the resin, distortion of laminae, deterioration of fiber/resin bond etc. These effects are collectively known as hydrothermal degradation, may be reversible on drying out the laminate and returning it to its initial condition, or permanent [5]. Because of the high performance laminates and composites, especially in aerospace, the effect of moisture/temperature environment has become an important aspect of composite material behavior. In this work the behavior of glass/carbon hybrid composites when exposed to varying temperature and moisture conditions is described. This is expected to be sensitive to moisture and temperature as the coefficients of expansion of glass and carbon fiber are different and the properties of glass/epoxy interface is sensitive to moisture.

2. WHY WE HAVE TAKEN THIS WORK?

The basic reason for working on such a topic arises from the fact that composites are vulnerable to environmental degradation. A moist environment, coupled with high or low temperature conditions is extremely detrimental for composites. There have been several efforts made by researchers in the last few years to establish the much needed correlation between the mechanical properties of the material and the moist environment or similar hydrothermal conditions, subjected to thermal shocks, spikes, ambient & sub ambient temperatures. But most research has been on the mechanical aspects rather than the physical & chemical interface and how this brings in change in the internal mechanical properties and affects a variety of other morphological changes.

The focus of our research has been to understand the physical changes that take place at the bonding interface between the fibers and the matrix, as it is of prime importance due to its link to the stress transfer, distribution of load, and it also governs the damage accumulation & propagation. This has wide significance in aerospace applications, because the aircraft components are exposed to harsh moist environment.

Hence our project work aims at the characterization of the hybrid FRP'S by DSC/SEM and to analyze the variation of Tg and flexural strength along with the mode of failure due to variation in moisture and temperature gradient.

3. LITERATURE SURVEY

3.1 COMPOSITES

A composite is combination of two materials in which one of the materials, called the reinforcing phase, is in the form of fibers, sheets, or particles, and is embedded in the other materials called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. Composites are used because overall properties of the composites are superior to those of the individual components. For example: polymer/ceramic composites have a greater modulus than the polymer component, but aren't as brittle as ceramics. The following are some of the reasons why composites are selected for certain applications:

- High strength to weight ratio (low density high tensile strength)
- High creep resistance
- High tensile strength at elevated temperatures
- High toughness

Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The strength of the composite depends primarily on[5,6]:

- Fiber matrix ratio or hybridization
- Fiber orientation
- Stacking sequence

In some cases when strength along with ductility is required multiple reinforcements are used for example brittle carbon or aramid fibers (Kevlar29 and kevlar49) are incorporated into the matrix along with ductile glass fibers to create a "**hybrid composite**" which clubs the good properties while mitigating the less desirable properties of both.

Composites can be broadly classified into 3 categories:

- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

3.2 ADVANTAGES OF COMPOSITE MATERIALS

- Stronger and stiffer than metals on a density basis For the same strength, lighter than steel by 80% and aluminum by 60%. Hence Superior stiffness-to-weight ratios.
- Highly corrosion resistant:

  Essentially inert in most corrosive environments. Benefits include lower maintenance and replacement costs.

- Tailor able thermal expansion properties

  Can be compounded to closely match surrounding structures to minimize thermal stresses

- Exceptional formability

  Composites can be formed into many complex shapes during fabrication, even providing finished, styled surfaces in the process.

- Low investment in fabrication equipment

  The inherent characteristics of composites typically allow production to be established for a small fraction of the cost that would be required in metallic fabrication.

- Good dimensional stability (extremely low coefficient of thermal expansion).
- Reduced Part Counts

  Parts that were formerly assembled out of several smaller metallic components can be fabricated into a larger single part. This reduces manufacturing and assembly labor and time.

3.3 APPLICATIONS

The composites industry has begun to recognize that the commercial applications of composites promise to offer much larger business opportunities than the aerospace sector due to the sheer size of transportation industry. Thus the shift of composite applications from aircraft to other commercial uses has become prominent in recent years [6]. Unlike conventional materials (e.g., steel), the properties of the composite material can be designed considering the structural aspects. The design of a structural component using composites involves both material and structural design. Composite properties (e.g. stiffness, thermal expansion etc.) can be varied continuously over a broad range of values under the control of the designer. Careful selection of reinforcement type enables finished product characteristics to be tailored to almost any specific engineering requirement.

Composites are used for the following purposes:

- Electrical and electronics
- Buildings and public works
- Road, rail, marine, cable, air, space transport
- General mechanical applications
- Sports and recreation
- Chemical, Oil and refinery industries
- Bio-mechanics applications

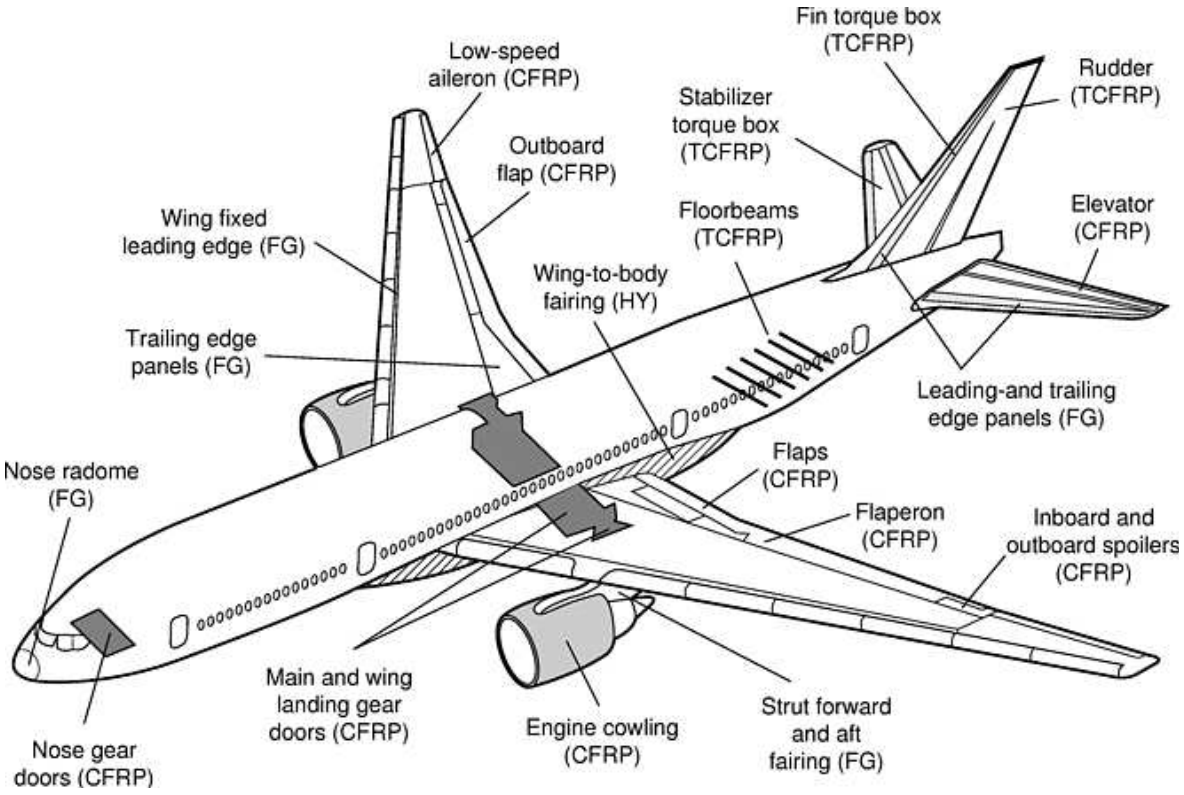


Fig 1:Showing Composites use on the Boeing 777-200[7]

3.4 HYBRID COMPOSITE

Hybrid composites are more advanced composites as compared to conventional FRP composites. Hybrids can have more than one reinforcing phase and a single matrix phase or single reinforcing phase with multiple matrix phases or multiple reinforcing and multiple matrix phases. They have better flexibility as compared to other fiber reinforced composites. Normally it contains a high modulus fiber with low modulus fiber.The high-modulus fiber provides the stiffness and load bearing qualities, whereas the low-modulus fiber makes the composite more damage tolerant and keeps the material cost low. The mechanical properties of a hybrid composite can be varied by changing volume ratio and stacking sequence of different plies [8,9].

3.4.1. ADVANTAGES OF HYBRID COMPOSITES

- They offer better flexibility in the selection of fiber and matrix materials, which helps in better tailoring of the mechanical properties. For example the modulus, strength, fatigue performance etc of glass reinforced composites can be enhanced by inclusion of carbon fibers
- Better wear resistance
- Low thermal expansion coefficient
- Combination of high tensile strength and high failure strain
- Better impact and flexural properties
- Reduced overall cost of the composite
- Low notch sensitivity
- Non catastropic

3.4.2. TYPES OF HYBRID COMPOSITE

There are several types of hybrid composites characterized as: (1) interply or tow-by-tow, in which tows of the two or more constituent types of fiber are mixed in a regular or random manner; (2) sandwich hybrids, also known as cor-shell, in which one material is sandwiched between two layers of another; (3) interply or laminated, where alternate layers of the two (or more) materials are stacked in a regular manner; (4) intimately mixed hybrids, where the constituent fibers are made to mix as randomly as possible so that no over-concentration of any one type is present in the material; (5) other kinds, such as those reinforced with ribs, pultruded wires, thin veils of fiber or combinations of the above.

3.4.3. APPLICATION OF HYBRIDS

- Helicopter rotor blades and drive shafts
- Ailerons and floor panels of aircrafts
- In automobile sector they are used in transmission units, chassis members, suspensions, and structural body parts of cars and lorries
- CFRP/ARP hybrids are used for making bicycle frames

- In sports industries Tennis racquets, fishing rods, skis, golf club shafts, yacht hulls, hockey sticks and paddles
- In medical world they are used for making orthoses.

3.5 STRENGH OF HYBRID COMPOSITE

The load bearing ability of hybrid composite is explained by following diagram.

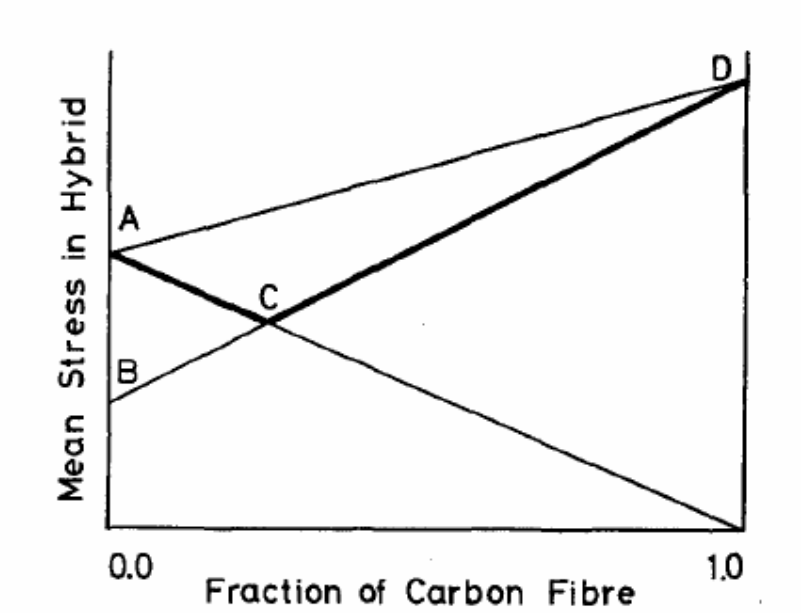


Fig 2: Strength of hybrid composite (consisting carbon, glass fiber and epoxy resin)

The horizontal axis depicts the fraction of carbon fibres in the structures which are all of identical total fibre content. The point A represents the tensile strength of the all-glass composite and D that of all-carbon composite. Since the carbon fibre has a lower elongation (0.01) than the glass (0.03), it may be expected that the first failure event will occur when the average strain in the composite exceeds the failure strain of the carbon failure. The line BD then represents the stress in the hybrid at which failure of the carbon fibre phase (CFP) will be expected. At low carbon fibre contents the glass fibre component (GFP) of the hybrid will be capable of carrying the extra load transferred to it by the failure of the carbon. The line AC is the ultimate strength of the hybrid in this condition. To the left of C the ultimate strength of the hybrid is determined by the glass, so that although the carbon will fail at BC the glass will

continue to sustain the stress up to AC, when it too will fail. To the right of C the carbon will fail at CD and the glass will not sustain the load transferred and will, therefore, also fail [10].

3.6 HYDROTHERMAL TREATMENT

Hydrothermal Diffusion usually takes place in presence of temperature and moisture gradients. In many cases water absorption obeys Fick's Law and diffusion is driven by the moisture concentration gradient between the environment and material producing continuous absorption until saturation is reached. The atoms migrate from region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise in temperature. The concentration gradient of moisture is developed due to the non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion. Epoxy resin absorbs water from the atmosphere from the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of water into all the material. The water absorbed is not usually in liquid form but consists of molecules or group of molecules linked by hydrogen bonds to the polymer. In addition water can be absorbed by capillary action along any crack which may be present or along the fiber-matrix interface [11, 12].

The Fickian diffusion process is influenced mainly by two factors:

(a) The internal (fiber volume fraction and its orientation)

(b) The external (relative humidity and temperature).

3.6.1. THEORY OF MOISTURE ABSORPTION

$$\mathbf{M = \frac{WEIGHT\,OF\,SPECIMEN\ -\ WEIGHT\,OF\,DRY\,SECIMEN}{WEIGHT\,OF\,DRY\,SPECIMEN} \times 100}$$

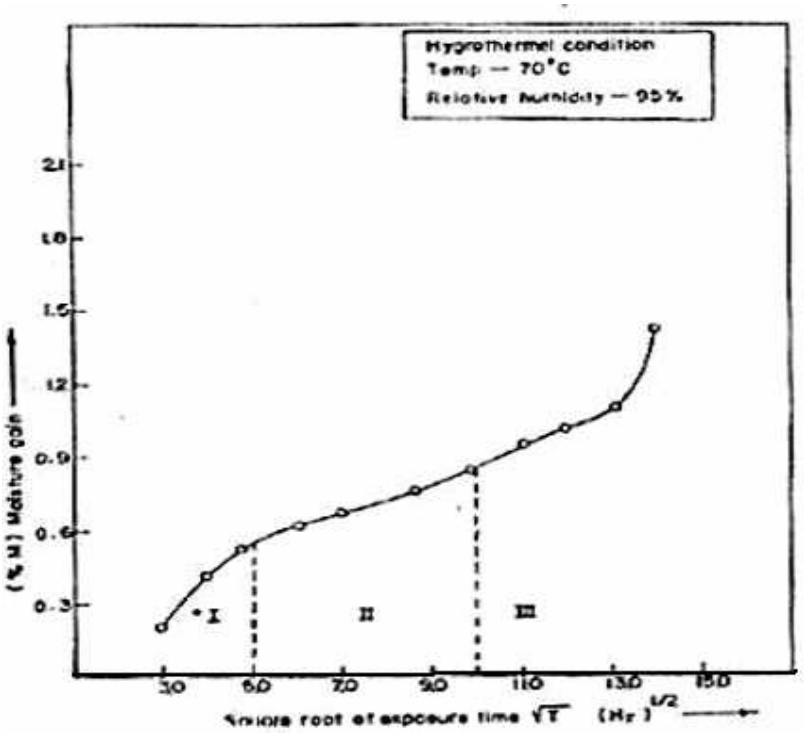


Fig 3: Different stages of moisture absorption

Description of the different stages in moisture absorption kinetics:

- **Stage 1** moisture absorption is Fickian
- **Stage 2** there is deviation from linearity (reaching saturation so there is decrease in slope)
- **Stage 3** Total non-Fickian pattern (there is a development of micro cracks which enable rapid moisture diffusion, so rapid increase in percentage of moisture.

NON-FICKIAN BEHAVIOR

Fickian behavior is observed in the rubbery state of polymers but often fails to diffusion behavior in glassy polymers. The deviation from Fickian behavior occurs when:-

(a) Cracks or delamination develops.

(b) Moisture diffusion takes place along the fiber matrix interface.

(c) Presence of voids in the matrix.

The nature of diffusion behavior whether Fickian or non Fickian depends on the relative rate at which the polymer structure and the moisture distributions change. When the diffusion rates are much slower than the rate of relaxation, the diffusion has to be Fickian. Non Fickian behavior pertains to the situations when the relaxation processes progress at a rate comparable to the diffusion process. Hydrothermal diffusion in polymeric composites is mostly Fickian type, but non-Fickian behavior is also common for glass/epoxy composite. Absorbed moisture in the composite certainly deteriorates the matrix dominated properties but he effect is more pronounced at higher temperatures and at lower strain rates. The ILSS values are the most affected property due to this moisture absorption.

3.7. 3-POINT BEND TEST

The FRP is subjected to three – point bending until the layers delaminates. When this occurs, the stiffness of the specimen as a whole decreases, this translates as a drop in load in the load - displacement curve. The three-point bend fixture should include two 5 mm diameter supports forming a 36 mm span and a 10 mm diameter load application roller set in the middle of the span. The crosshead speed is 1mm/min unless otherwise specified. Test should be performed at 23 ± 2 ℃. The three point bending flexural test provides values for the modulus of elasticity in bending E_B The flexural stress σ_f , flexural strain ε_f, and the flexural stress- strain response of the material. The main advantage of a three point flexural test is the ease of specimen preparation and testing. However, this method has also got some disadvantages such as the results of testing method are sensitive to specimen and loading geometry and strain rate [13].

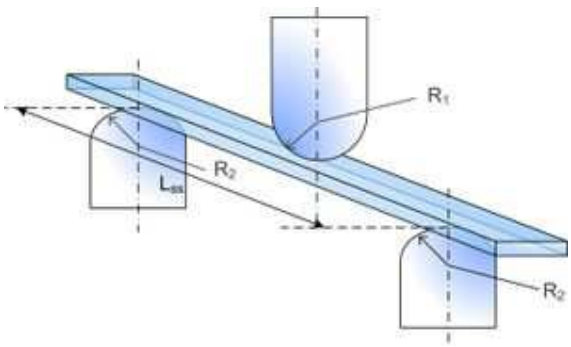


Fig 4: Flexural test setup

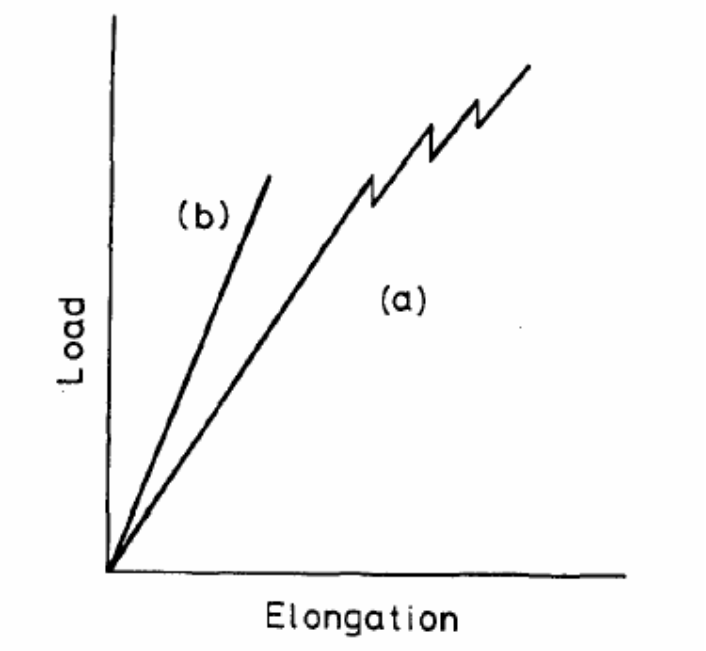


Fig 5: (a) Hybrid composite (consisting glass fiber, carbon fiber and epoxy) (b) Carbon fiber composite

Load-elongation curves (displacement controlled loading) for these two conditions are shown in Fig. a and b. In Fig. a failure in the CFP is marked by a load drop. On further extension the load continues to rise but there is a stiffness reduction due to transfer of load from the broken CFP to the GFP. Several failure events may occur in the CFP before final catastrophic failure of the GFP. In Fig. b the first CFP failure initiates a cata-strophic failure sequence in the whole composite [10].

Calculation of the flexural stress, flexural strain and young's modulus :

FLEXURAL STRESS:

$$\sigma_f = \frac{3PL}{2bd^2}$$

FLEXURAL STRAIN

$$\epsilon_f = \frac{6Dd}{L^2}$$

YOUNG'S MODULUS

$$E_B = \frac{L^3 m}{4bd^3}$$

- σ_f = Stress in outer fibers at midpoint, [MPa]
- ε_f = Strain in the outer surface [%]
- E_f = Modulus of elasticity in bending [MPa]
- P = load at a given point on the load deflection curve [N]
- L = Support span [mm]
- b = Width of test beam [mm]
- d = Depth of tested beam [mm]
- D = maximum deflection of the center of the beam [mm]
- m = Slope of the tangent to the initial straight-line portion of the load deflection curve [N/mm]

INTER LAMINAR SHEAR STRENGTH

Inter laminar shear strength may be defined as the resistance of a layered composite to internal forces that tend to induce relative parallel motion to and between the layers [14].

ILLS = 3*P/4*b*h

Where p=maximum load

b=width of specimen

h=thickness of specimen

3.8. EFFECT OF HYDROTHERMAL TREATMENT ON GLASS TRANSITION TEMPERATURE T_g

Glass transition temperature (Tg) of thermo set matrix in composites is very important property because it defines the critical service temperature of the component and consequently their applications. For practical applications they are used at a temperature below their Tg i.e. in the glass state. When materials are exposed to hydrothermal environment, the Tg usually decreases and therefore, the service temperature of the material changes. Moisture absorption by epoxy matrix composites has plasticizer effect, as reduction of Tg of the matrix. This effect is usually reversible when water is removed but exposure to high temperature can produce irreversible effects, which is attributed to the chemical degradation of the matrix and attack on the fiber/matrix interface. This causes increase of internal voids of the entangling polymer chain, promoting chain expansion and the micro-cracks formation into the polymer matrix. There are many factors on which moisture absorption depends such as temperature, fiber volume fraction, reinforcement orientation, fiber nature (i.e. permeability, polarity, and density), and area of exposed surfaces, diffusivity and surface protection [15, 16].

3.8.1. DSC (DIFFERENTIAL SCANNING CALORIMETRY)

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. There are two types of DSC systems in common use. DSC is used to determine the heat flow associated with material transitions as a function of time and temperature or changes in heat capacity using minimal amount of material. The technique provides quantitative and qualitative data on endothermic and exothermic processes of material during physical transitions caused by phase changes, melting, oxidation, and environmental degradation. The technique involves slowly heating a small sample of material and measuring the heat absorbed or emitted by the samples as a function of temperature compared to a reference material. DSC is used to measure $_{Tg}$.[17].

Fig 6: DSC to measure Glass transition temperature

3.9. SEM ANALYSIS

SEM studies are done to know the gross hydrothermal, thermal and cryogenic conditioning on the fiber matrix interface adhesion characteristics and to confirm the principal modes of failure: delamination, matrix cracking, void formation, fiber breakage.

Fig 7: SEM (JEOL jsm-6480lv), NIT ROURKELA

4. EXPERIMENTAL PROCEDURES

4.1. General overview

The hybrid composites were fabricated by hand lay-up method. The composites sheets were fabricated from E glass fiber, carbon fiber and resin matrix. The resin used was epoxy resin. The weight fraction of composites was maintained at 50% fiber and 50% resin. Number of plies for each fiber taken was eight i.e. total number of plies used in hybrid composite are sixteen. After the hybrid composites fabrication moisture removal was done in oven maintain temperature at 60^0c. Then samples were subjected to hydrothermal treatment followed by thermal and cryogenic treatment. Bulk of the work was carried out under hydrothermal conditions. Two groups of samples were prepared. The first group is initially subjected to hydrothermal treatment which is further divided into two sections: one is for thermal treatment and another is for cryogenic treatment. The second group is studied without any treatment. The samples in all cases were tested by three point bend test method. This apart, SEM micrographs were also taken for various conditions along with DSC thermographs. The results got from various tests are correlated.

4.2. Fabrication of specimen

The fiber piles were cut to size from the woven fiber cloth. The appropriate numbers of fiber plies were taken: eight for each. Then the fibers were wighed and accordingly the resin and hardeners were weighed. Epoxy and hardener were mixed by using glaas rod in a bowl. Care was taken to avoid formation of bubbles. Because the air bubbles were trapped in matrix may result failure in the material. The subsequent fabrication process consisted of first putting a releasing film on the mould surface. Next a polymer coating was applied on the sheets. Then fiber ply of one kind was put and proper rolling was done. Then resin was again applied, next to it fiber ply of another kind was put and rolled. Rolling was done using cylindrical mild steel rod. This procedure was repeated until eight alternating fibers have been laid. On the top of the last ply a polymer coating is done which serves to ensure a god surface finish. Finally a releasing sheet was put on the top; a light rolling was carried out. Then a 20 kgf weight was

applied on the composite. It was left for 24 hrs to allow sufficient time for curing and subsequent hardening.

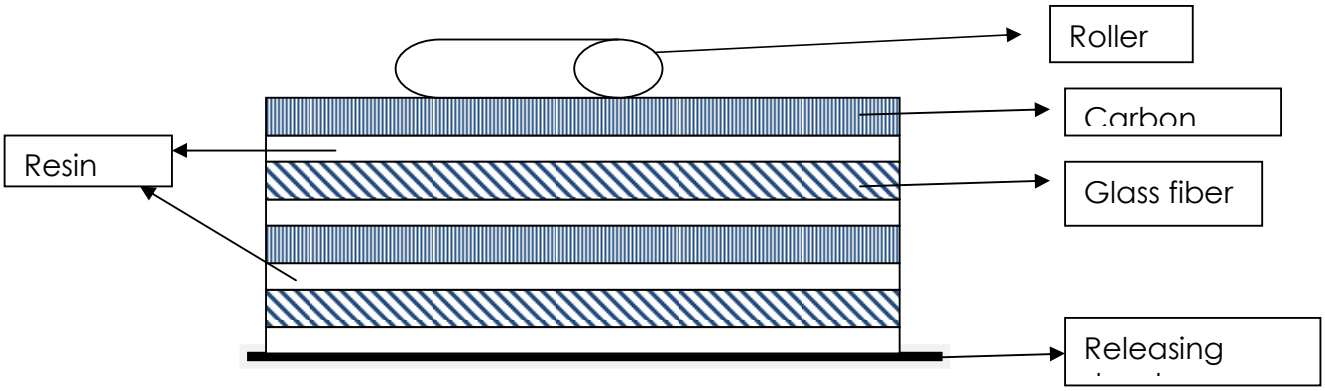


Fig 8: A schematic representation of the hand lay- up process

Once the basic composite was made it has to be cut to proper size (as per ASTM specification for three point bend specimen). The specimens were cut using a diamond tipped circular cutting saw. Then samples were conditioned hydrothermally.

4.3. Experimental set ups

The samples were prepared, dried in oven for the purpose of moisture removal at 60^0c. Oven was used for the hydrothermal treatment. Once the chamber was switched on, sufficient time gap was allowed till the required temperature was attained (TEMP=60^0c). Samples were kept in glass beaker containing distilled water, put inside the chamber and subsequently removed after predetermined time periods (24hrs, 48hrs, 72hrs, 96hrs, and 120hrs). After hydrothermal treatment was over each specimen was weighed by an electronic weighing machine. The samples were taken out, some kept for thermal treatment and some for cryogenic treatment. The thermal treatment chamber was oven which is maintained at 50^0c. The cryogenic treatment was done at a temperature of -40 ^{0}c in a double compressor fitted deep freezer. Cares have been taken during putting and taking out the samples from into or out of the chamber. The testing was performed very soon after removal of samples from the treatment

chambers. The mechanical characterizations of samples were done using three point bend tests at a cross Head velocity of 2mm/min and compared with three point bend results of as cured samples.

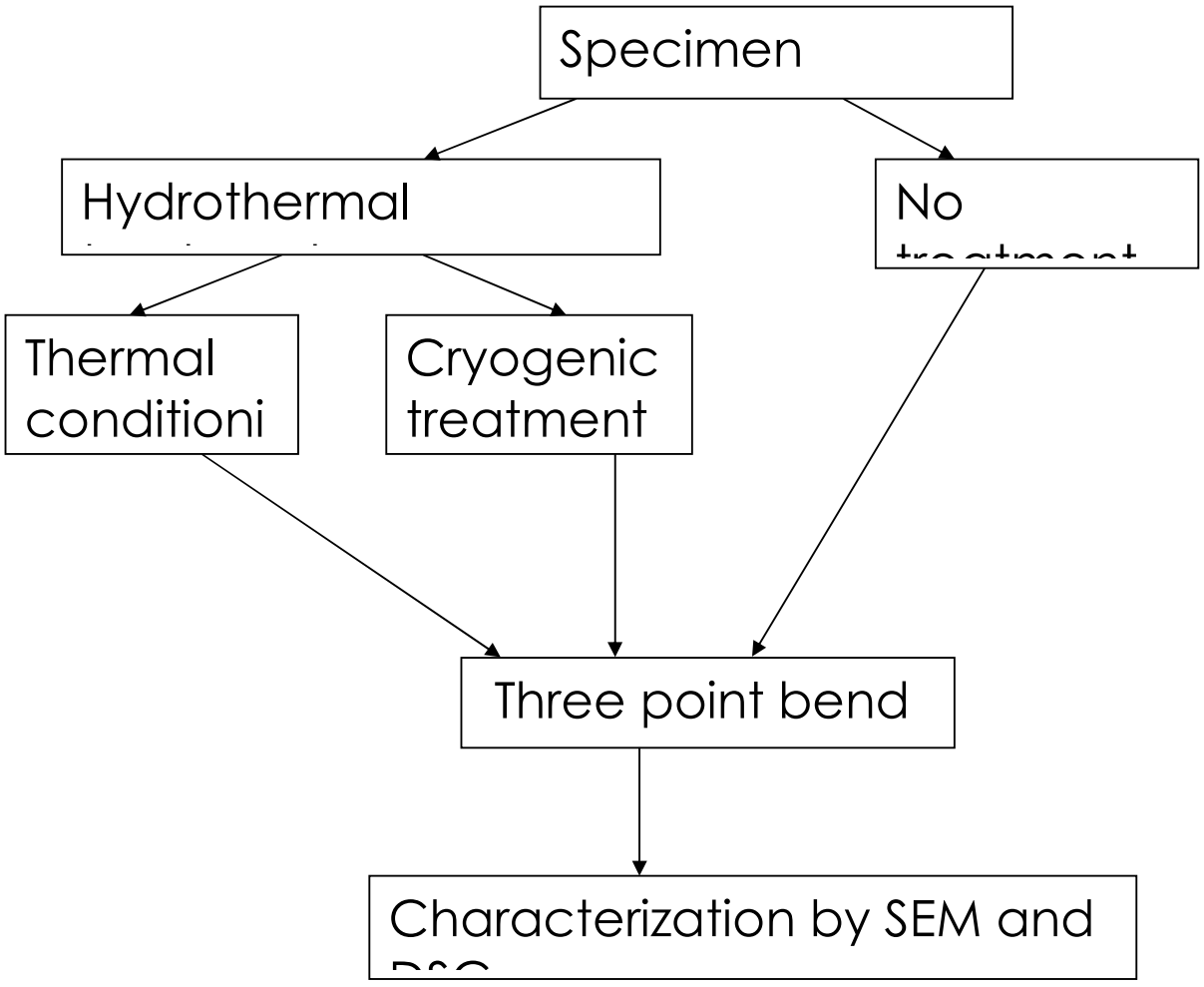
Fig 8: Hydrothermal chamber

4.4. Characterization

Characterization technique involves scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The three bend tests were carried out in an INSTRON 1195 machine to ascertain ILSS value of hybrid composites. The breaking load obtained in the process was noted. Then the fractured samples were analysed through scanning electron microscopy. First the samples were given a surfacial carbon coating (to make it conducting). Then they were loaded into a sample holder, and SEM micrographs were taken at various

points. DSC of samples was carried out to ascertain the glass transition temperature (T_g) of composites.

Structure of the work



5. RESULTS AND DISCUSSION

5.1. Moisture absorption

Sample no	Initial wt(gms)	Final wt(gms)	%moisture absorbed (wt %)	Average moisture absorbed (wt %)	Time in hrs
1	8.17	8.230	0.7344	0.6979	24
2	9.07	9.130	0.6615		
3	8.34	8.410	0.8392	0.8762	48
4	8.76	8.840	0.9132		
5	6.84	6.900	0.8772	0.8876	72
6	9.20	9.270	0.898		
7	7.26	7.33	0.8264	0.914	96
8	7.98	8.060	1.0026		
9	8.87	8.950	0.9019	0.9423	120
10	9.15	9.24	0.9836		

TABLE NO 1: Samples treated hydrothermally varying with time (Hrs)

These above results can be formulated in the forma of a table as under

SI NO	No. of hours of hydrothermal treatment	Average moisture absorbed (wt %)
1	24	0.6979
2	48	0.8762
3	72	0.8876
4	96	0.914
5	120	0.9423

TABLE NO 2: Average moisture (wt%) absorbed with number of hours of hydrothermal treatment

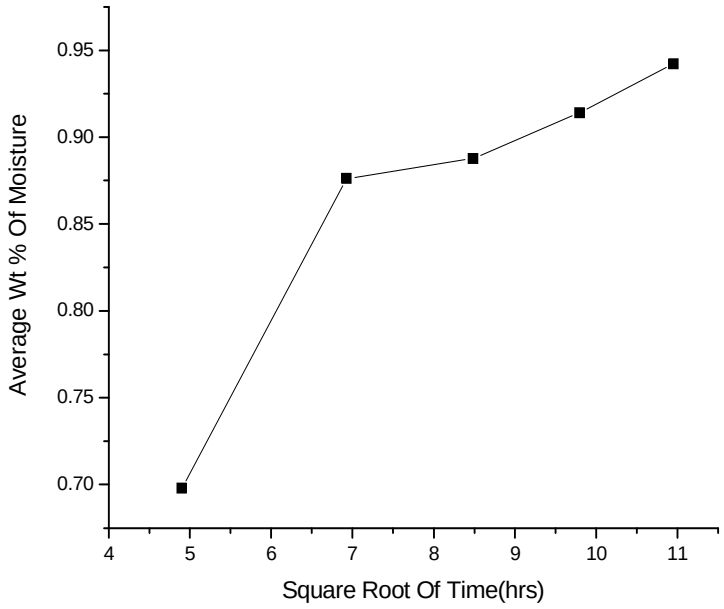


Fig 9: Average wt% of moisture vs square root of time(hrs)

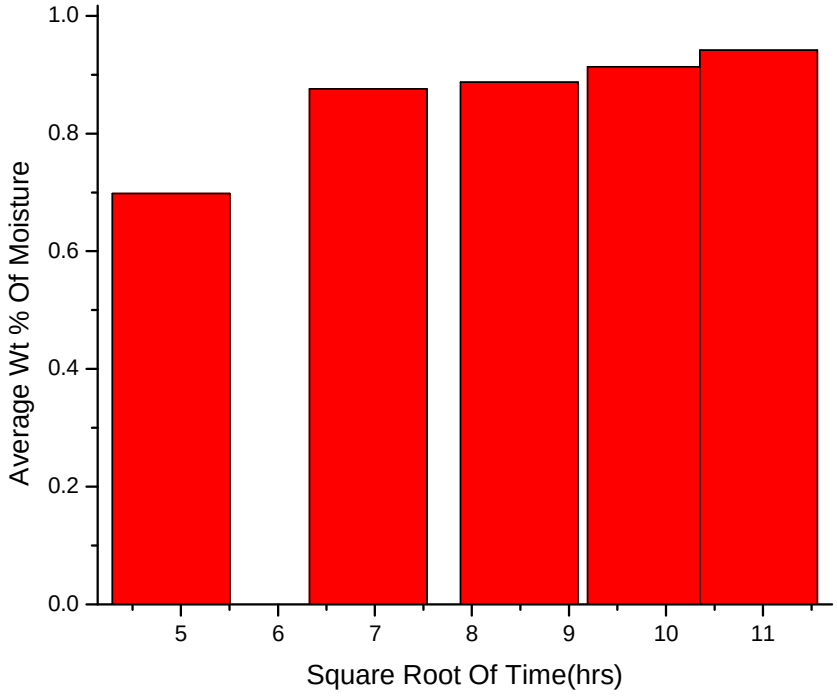


Fig 10: Bar representation of average wt% of moisture pick up with square root of time (hrs)

Interpretation

From the above graph we can interpret the following points.

- Initially the rate of moisture absorption is high. This is due to the presence of free spaces in the composites. The moisture absorption obeys fick's law i.e. the fickian curve is obtained.
- After a specific time the rate of moisture absorption decreases gradually. This is due to the saturation of the matrix i.e. the moisture absorbed is sufficient enough to fill the spaces and very less moisture is required.
- So we can conclude that moisture absorption is highest in the beginning and the gradually goes on decreasing after a specific interval of time due to saturation [18].

5.2. Effect of Moisture Content and time on ILSS of thermally treated samples

Sample no	Time (hrs) of treatment	Moisture content (wt %)	ILSS(MPa)
As cured	0	0	32.746
2	24	0.6615	33.74
4	48	0.9132	30.47
6	72	0.898	28.45
7	96	0.82	31.63
10	120	0.98	29.48

TABLE N0-3: showing ILSS of thermally treated samples with variations in time and moisture content

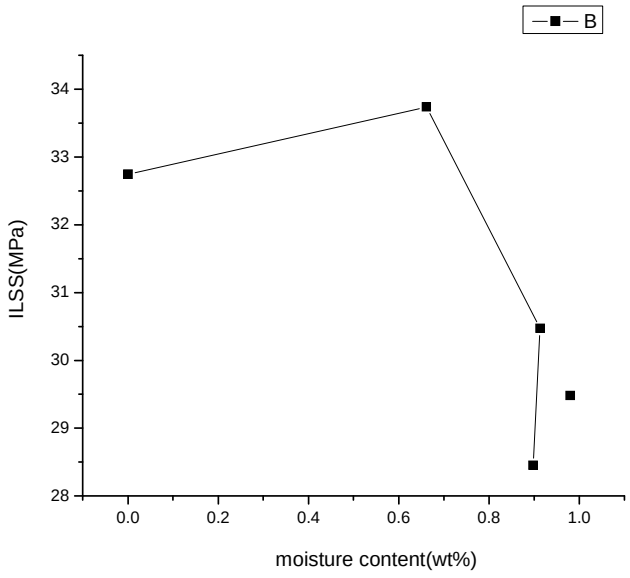


Fig11: ILSS (MPa) vs moisture content (wt %)

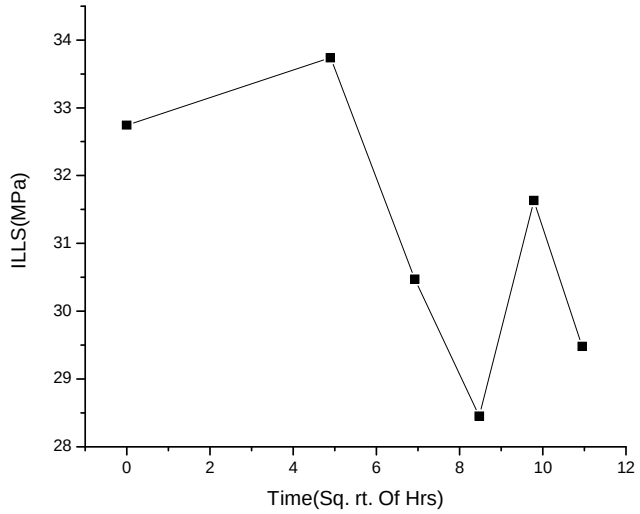


Fig 12: ILSS(MPa) vs square root of time (in hrs)

5.3. Effect of Moisture Content and time on ILSS of cryogenic treated samples

Sample No	Time (hrs)of treatment	Moisture content (wt %)	ILSS(MPa)
As cured	0	0	32.746
1	24	0.7344	40.97
3	48	0.8393	30.37
5	72	0.8772	29.99
8	96	1.0025	32.32
9	120	0.9019	37.32

Table No 4: showing ILSS of cryogenic treated samples with variations in time and moisture content

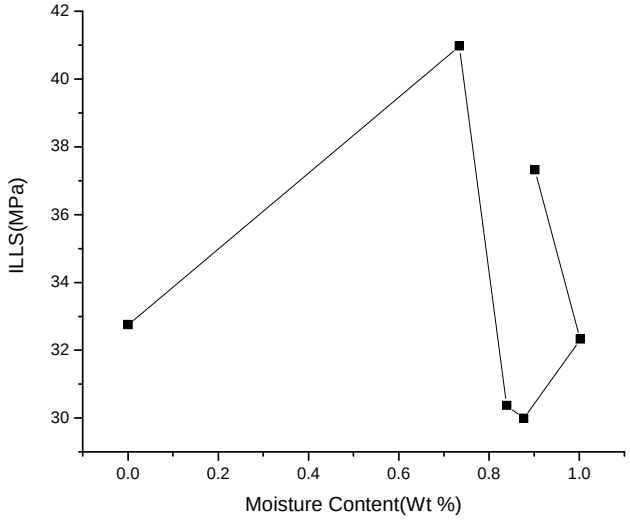


Fig 13: ILSS (MPa) vs Moisture content (in wt %)

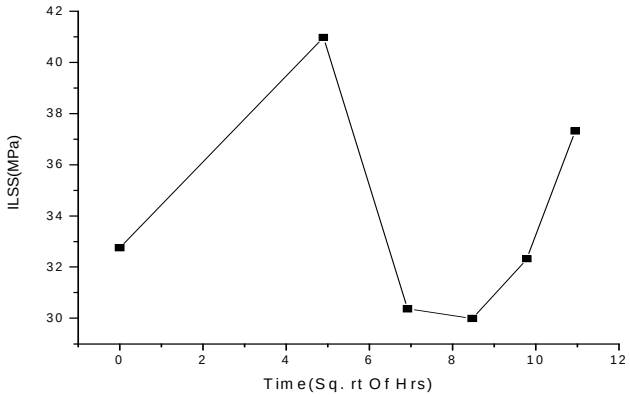


Fig 14: ILSS (MPa) vs square root of time (hrs)

Interpretation

From the above graph we came to the following inferences:

- Initial moisture level increases the ILSS values. This may be due to the relief of the stresses induced during curing.

- There results swelling stresses due to the expansion of the matrix by moisture absorption---these are opposite in nature to the curing stresses. Hence ILSS increases.
- With subsequent moisture absorption, ILSS decreases because the adhesion between the molecules is lowered [19].
- Then increase in ILSS is due to hydrolysis of polymer chains. There is breakage of covalent bonds and the absorbed water molecules form strong hydrogen bonds with the hydrophilic groups of the epoxy network. Water with double hydrogen bonds acts as a physical crosslink. Due to the formation of hydrogen bonds, there is an increase in Tg and ILSS.

5.4. Characterization by DSC

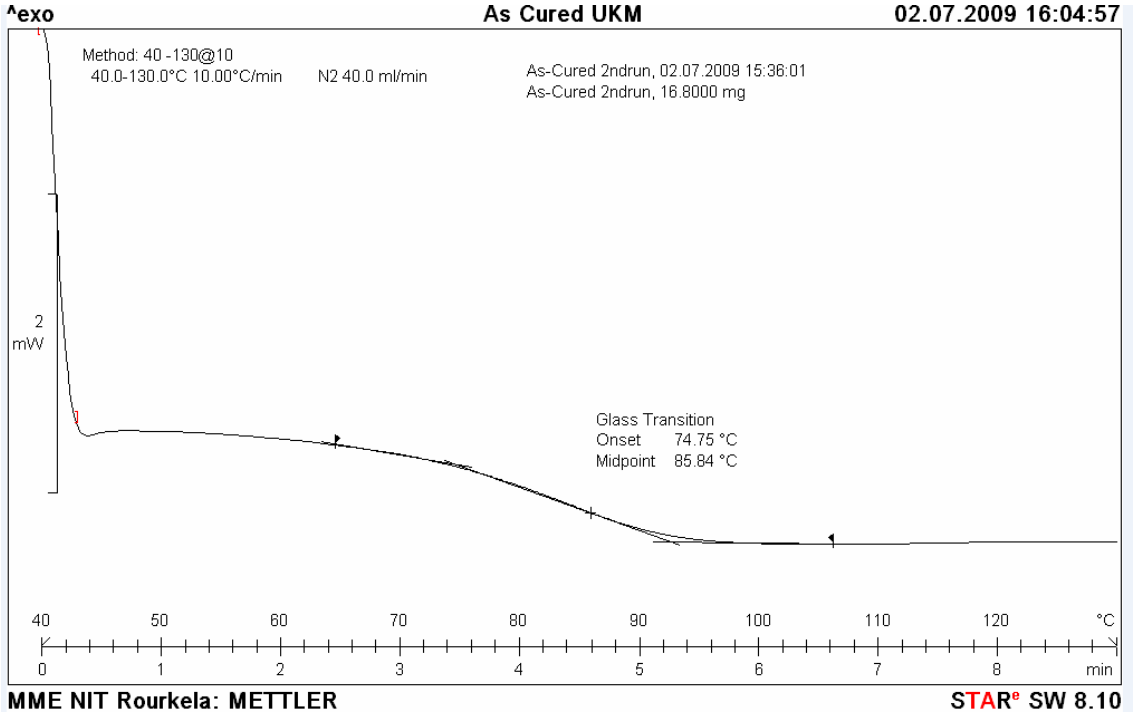


Fig 15: DSC of As cured sample

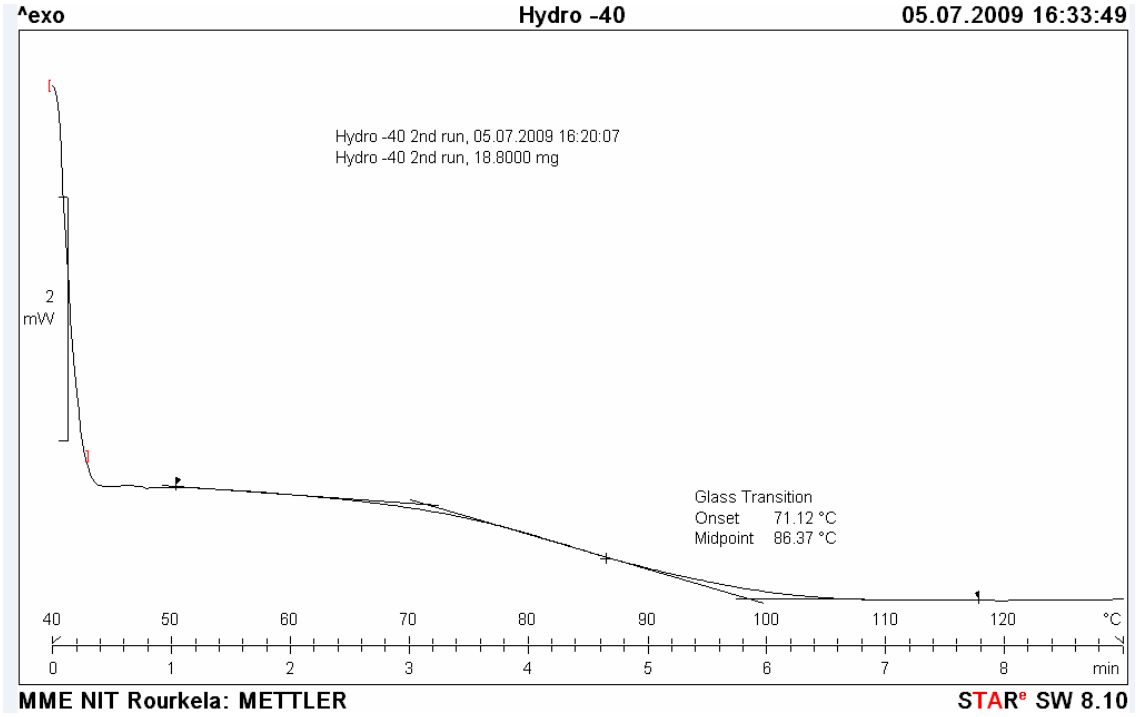


Fig 16: DSC of cryogenic sample

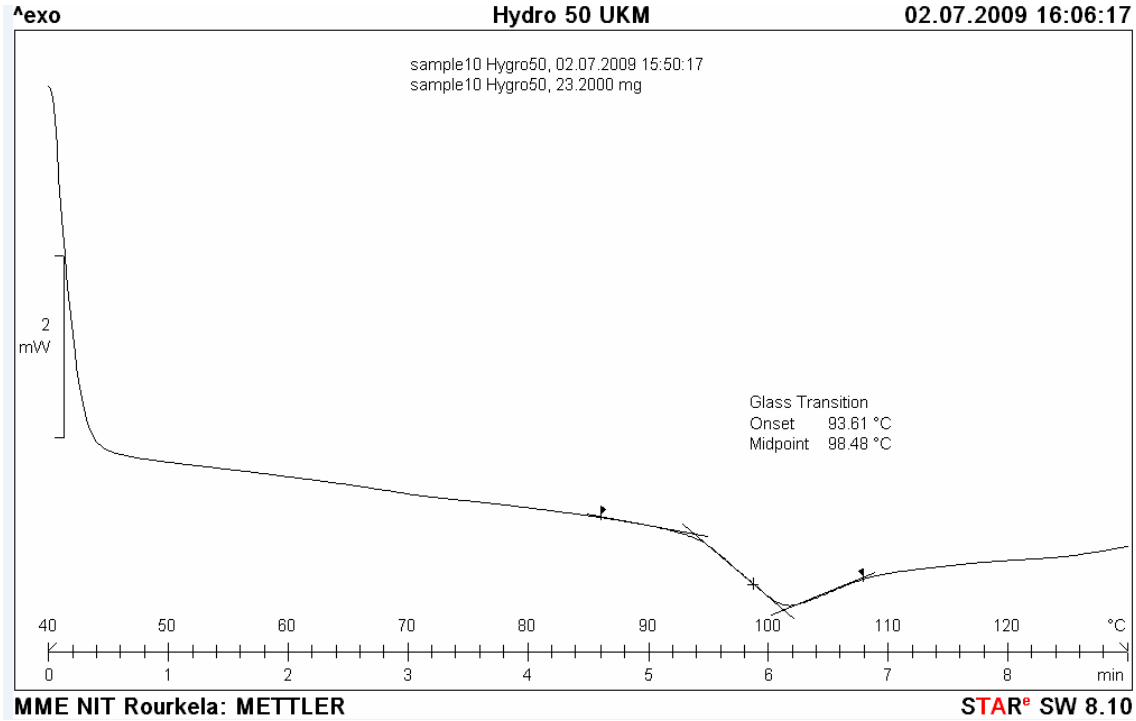


Fig 17: DSC of thermally treated sample

From the graphs it is clear that as cured sample has the highest T_g and thermally treated sample has lowest T_g.

	As cured	Thermally treated	Cryogenic treated
Moisture content (%)	NO moisture	0.898	0.8772
Transition temperature(^{0}c)	85.84^{0}c	98.48^{0}c	86.37^{0}c

Table No-5: Transition temperature (T_g) vs moisture content

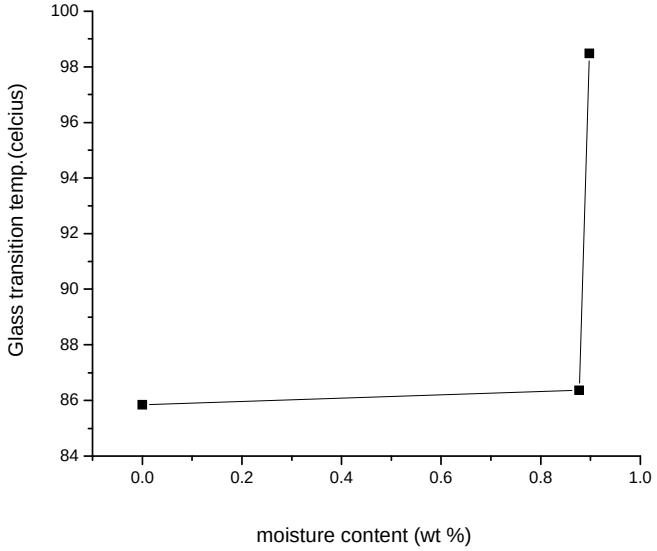


Fig 18: Glass transition temp (T_g) vs moisture content (wt %)

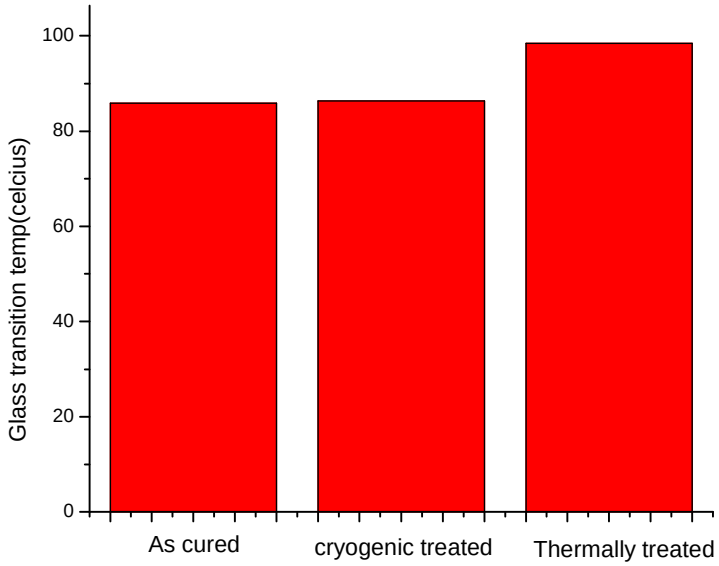


Fig 19: Bar representation of Glass transition temp (^{0}c) with variation of treatment

5.4.1. VARIATION OF Tg WITH MOISTURE CONTENT

We see that with an increase in the number of hours of hydrothermal treatment, there is an increase in Tg. Here the number of hours of treatment given is low hours hydrothermal treatment. So in this case hydrolysis predominates plasticization. Due to hydrolysis there will be scission of polymer chains. There is breakage of covalent bonds and the absorbed water molecules form strong hydrogen bonds with the hydrophilic groups of the epoxy network. Water with double hydrogen bonds acts as a physical crosslink. Due to the formation of hydrogenbonds, there is an increase in Tg.The presence of water at the interphase causes the covalent chemical bonds between the silane coupling agents and the glass surface to transform into strong physical interactions via formation of hydrogen bonds between the glass surface , water molecules and network of silane coupling agents.

The formation of hydrogen bonds may be represented as shown below:

H-O-H + P1 (polar group) = H-O-H----- P1 (Single hydrogen bond)

H-O-H + P2 (polar group) = H-O-H----- P2 (Single hydrogen bond)

H-O-H-------P1 + H-O-H--------P2 = P1------H-O-H------ P2 (Double hydrogen bond)

5.4.2. EFFECT OF Tg ON MECHANICAL PROPERTIES

Tg is of great importance in use of polymeric materials. It is used for evaluating the flexibility of a polymer molecule and the type of response the polymeric material would exhibit to mechanical stress. The **Tg** value of a polymer, therefore decides whether a polymer at the use temperature will behave like rubber or plastic. Polymers above their **Tg** will exhibit a delayed elastic response (viscoelasticity), while those above **Tg** will exhibit dimensions stability. The knowledge of Tg will give an idea about the correct processing temperature of the polymer. General commonsense prevails that higher the **Tg** better the mechanical properties. When we talk of effect of moisture absorption on **Tg, we** generally talk about extremely high hour hydrothermal treatment, because in real life, the FRP structures are subjected to many many hours of moisture absorption. From our experimental point of view, we have done hydrothermal treatment for 24 hrs to 120 hours. This is extremely low hour treatment. Here hydrolysis dominates, instead of plasticization. We see that hydrolysis increases **Tg** and also ILSS initially. Hence we are tempted to assume that there is enhancement of mechanical properties. But this is misleading, since this does not happen in case of engineered structures. In case of engineered structures, there is plasticization of matrix when there is moisture absorption for long hours. This plasticization goes on increasing as the number of hours goes on increasing; we know that plasticization leads to decrease in Tg and deterioration of matrix.

5.5. Microstructural characterization by SEM

Water absorption in epoxy matrix composites can take place through matrix interface, cracks and voids in composites. The water distribution inside the material never attains a steady state. It changes continuously, the water concentration depending on time. It affects the

mechanical properties of the composite.

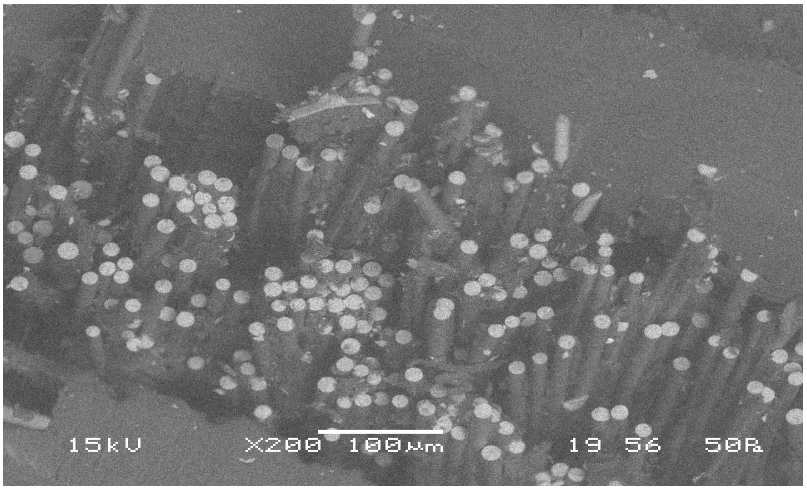


Fig 20: As cured sample: showing no defect, failure modes

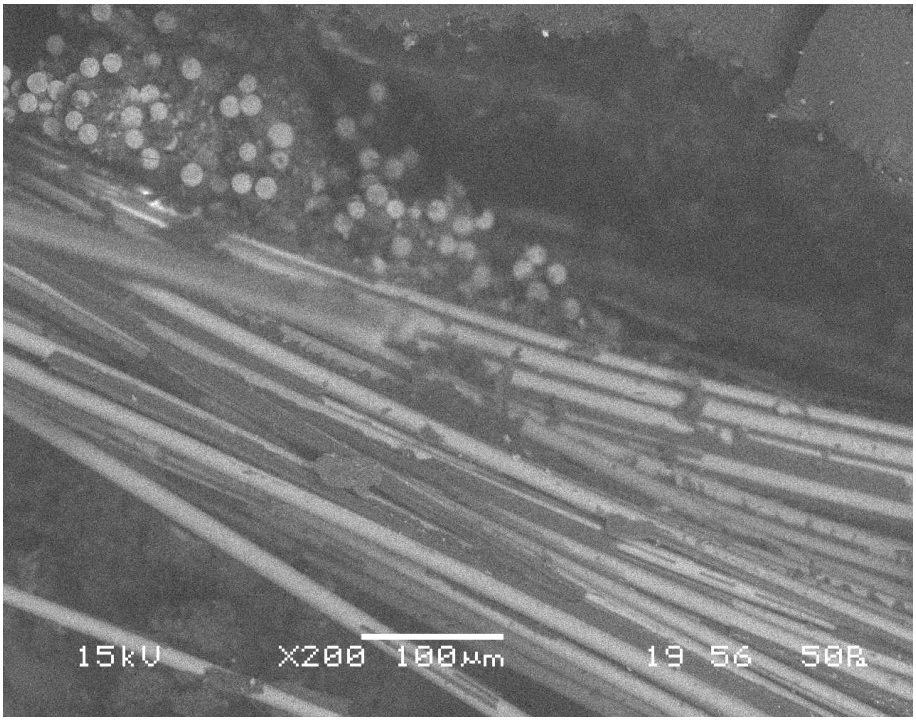


Fig 21: Showing matrix cracking fiber brekage

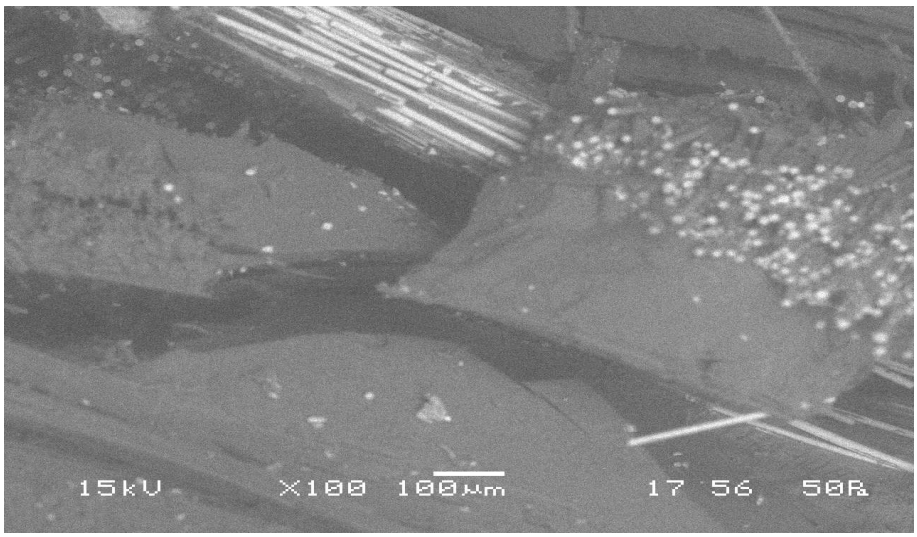


Fig 22: Showing Matrix cracking some fiber pullout

The principal modes of observed are:

- Delamination
- Matrix cracking
- Debonding

DELAMINATION

Delamination is the separation of plies of a laminate. The delamination in composites is caused by interlaminar stresses produced by out of plane loading (e.g., impact) eccentricities in load paths or discontinuities in the structure. Matrix cracking in off-axis plies may generate interlaminar stresses to promote delamination. REIFSNIDER estimate that in quasi isotropic laminates, these interlaminar stresses occur near the crack tip of the matrix. These interlaminar stresses tend to cause local delamination that grows along ply interfaces near

matrix cracks. The magnitude depends upon the materials used, stacking sequence, laminate shape, or type of loading.

EFFECTS OF DELAMINATION

- Reduction in stiffness
- Reduced strength
- Reduced rate of resistance to fatigue

MATRIX CRAKING

Matrix cracking is characterized by microscopic cracks that form predominantly in the matrix areas of laminate under loading. Their orientation may be in any direction depending on the applied stress. In multidirectional laminate, matrix cracks will appear first in the weakest ply then subsequently with increase in stress propagates to the strong layers. Matrix cracks are initiated early in the process of fatigue. The stacking sequence and the stress distribution near the fiber matrix interface play an important role in failure by matrix cracking. Moisture absorbed also contributes towards matrix cracking, due to difference in coefficients of volume expansion of fiber and matrix stresses are generated, which is accountable for matrix cracking [20].

DEBONDING

Debonding occurs due to the interfacial shear stress components. The extent of debonding is decided by the boding between the matrix and the fibers. High interfacial bond strengths will permit little or no fiber matrix interfacial debonding. In contrast with low bond strength may exhibit large areas of interfacial debonding that combines with or intensifies other damage mechanisms to speed up failure [20].

6. CONCLUSION

Any composite material, when exposed to hydrothermal environment, always absorbs moisture, and this leads to deterioration of mechanical properties.

Following conclusions were made:

- The amount of moisture absorbed increases with increase in time of hydrothermal treatment. Initially the rate of moisture absorption is high. This is due to the presence of free spaces in the composites. The moisture absorption obeys fick's law i.e. the fickian curve is obtained. After certain time the rate of moisture absorption decreases gradually.
- The ILSS values increase initially & then decreases increase in % of moisture. This may be due to the relief of the stresses induced during curing.
- With subsequent moisture absorption, ILSS decreases because the adhesion between the molecules is lowered.
- Then increase in ILSS is due to hydrolysis of polymer chains. There is breakage of covalent bonds and the absorbed water molecules form strong hydrogen bonds with the hydrophilic groups of the epoxy network. Water with double hydrogen bonds acts as a physical crosslink. Due to the formation of hydrogen bonds, there is an increase in Tg and ILSS.

Also by focusing on the physical changes that take place at the interface, we can infer about the many causes for change or deterioration in the mechanical properties. The interface monitoring can give the relationship between % moisture absorbed and the effect on the glass transition temperature.

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